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RESEARCH MEMORANDUM

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MIXED BUTYL MERCAPTANS WITH VARIOUS WHITE FUMING
NITRIC ACIDS USING MODIFIED OPEN-CUP AND
SMALL-SCALE ROCKET ENGINE APPARATUS

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Cleveland, Ohio

NATIONAL ADVISORY COMMITTEE
FOR AERONAUTICS

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IGNITION-DELAY DETERMINATIONS OF FURFURYL ALCOHOL AND MIXED BUTYL
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SUMMARY

Ignition-delay determinations of furfuryl alcohol and mixed butyl mercaptans with various white fuming nitric acids were made at several temperatures utilizing a modified open-cup apparatus and a small-scale rocket engine of approximately 50-pounds thrust.

Approximate linear relations were obtained when the logarithm of ignition delay was plotted against the reciprocal of absolute temperature for furfuryl alcohol and white fuming nitric acid (16 percent water) in the small-scale engine and for mixed butyl mercaptans and white fuming nitric acid (2 percent water) in the modified open-cup apparatus.

Zero temperature coefficients of ignition delay were obtained for furfuryl alcohol and white fuming nitric acid (2 percent water) in both apparatus for the temperature ranges investigated.

INTRODUCTION

The Bureau of Aeronautics, Department of the Navy, requested the Lewis laboratory to determine temperature - ignition delay relations of the following propellant combinations: (1) furfuryl alcohol and white fuming nitric acid; and (2) mixed butyl mercaptans and white fuming nitric acid.

As part of an effort to establish a generalized theory of ignition of self-igniting rocket propellants, the Bureau is attempting to derive empirical relations from ignition-delay data reported by various organizations. In order to simplify the task, the Bureau occasionally requests these laboratories to conduct and submit the results of certain control experiments.

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A portion of the work requested has already been reported in reference 1. These results, along with new complementary experimental results obtained to complete the program, are described herein.

APPARATUS AND PROCEDURE

The modified open-cup apparatus, one of the two apparatus used in this investigation, is shown in figure 1. It consists of a test-tube reaction vessel containing a small amount of oxidant in which a sealed glass ampule holding the fuel is immersed. The ignition delay is taken as the time interval between the crushing of the ampule and the commencement of a continually persistent flame. The apparatus and its operation are described in detail in references 2 and 3.

The other apparatus is a small-scale rocket engine of approximately 50-pounds thrust and is shown in figure 2. The ignition delay is the time interval between the meeting of the propellant jets in the transparent combustion chamber and the appearance of flame, and is measured by a high-speed motion-picture camera. In their present forms, the apparatus and operating procedure are essentially the same as those described in detail in reference 4. All runs reported herein were made with a propellant injection pressure of 450 pounds per square inch gage.

PROPELLANTS

Chemically pure furfuryl alcohol was used in the experiments described in this report. The mixed butyl mercaptans was taken from a batch of fuel obtained from the Naval Air Rocket Test Station for use in a program described in reference 1.

The nitric acids were white fuming acids meeting USAF Specification No. 14104, mixtures of these acids with various amounts of water, and anhydrous nitric acid.

RESULTS AND DISCUSSION

Furfuryl Alcohol - White Fuming Nitric Acid

Modified open-cup. - In the modified open-cup apparatus, 12 runs were made at temperatures from 22° to 2° C with furfuryl alcohol and white fuming nitric acid containing 2 percent water by weight. The results of these experiments are shown in table I. A plot of ignition delay against temperature is shown in figure 3.

In the temperature range investigated, the average ignition delay was constant at about 25 milliseconds. With one exception, the actual values ranged from 21 to 29 milliseconds, the maximum deviation being 4 milliseconds from the average. Of course, a linear zero-slope relation is also obtained when the logarithm of ignition delay is plotted against the reciprocal of absolute temperature (fig. 4). This method of plotting the data affords the opportunity to see whether or not the ignition delay behaves according to the simple Arrhenius reaction-rate equation.

In this series of runs, propellant viscosity had no significant effect on ignition delay since 20 centistokes, the minimum value at which viscosity appears to affect mixing efficiency in the modified open-cup apparatus (ref. 1), was not exceeded.

In a series of 14 runs conducted earlier at -40° C with furfuryl alcohol and a white fuming nitric acid containing 2.6 percent nitrogen dioxide and less than 1 percent water by weight, the ignition delays ranged from 30 to 72 milliseconds with 48.5 milliseconds as the average (table I). The higher delays at this temperature may be attributed to the high fuel viscosity (219 centistokes) and the low initial reaction rate. The scatter in the results at this temperature may be due to unreproducible mixing conditions that occur with the supercooled viscous fuel.

Small-scale engine. - In the small-scale rocket-engine apparatus, 14 runs were conducted at temperatures ranging from 50° to -40° C with furfuryl alcohol and white fuming nitric acids containing 2, 5, and 16 percent water by weight. One run was also made at -40° C with an acid containing less than 1 percent water by weight. The results of these experiments are shown in table II. A plot of the data showing ignition delay as a function of temperature is shown in figure 5.

With the acid containing 2 percent water, the ignition delay from 50° to -20° C was 16 ± 3 milliseconds. The temperature coefficient of ignition delay appeared to be zero in this range of temperatures. Except for the run at 20° C (run 314), the combustion-chamber pressures were between 270 and 300 pounds per square inch gage.

With the acid containing 5 percent water, the ignition delays ranged from 18 milliseconds at 30° C to 70 milliseconds at -40° C. The results of the run at -11° C (run 296) are questionable, because its weak ignition point, as seen on the high-speed film record, indicates a poor oxidant-fuel ratio due to improper bursting of the propellant-tank disks. No chamber pressures were available to check this observation. In the other runs, the combustion-chamber pressures decreased as the propellant temperatures decreased; they ranged from 200 pounds per square inch gage at 30° C to 80 pounds per square inch gage at -40° C.

With the acid containing 16 percent water, the ignition delays ranged from 43 milliseconds at 19° C to 225 milliseconds at -20° C. Weak ignitions and combustions were characteristic of all these runs. The chamber pressures were all low and ranged from about 190 to 110 pounds per square inch gage as the temperatures decreased from 19° to -20° C.

As reported previously (ref. 4), the one run made with acid containing less than 1 percent water yielded a delay of about 54 milliseconds at -40° C.

In every case in these series of furfuryl alcohol runs, a heavy carbonaceous residue was found deposited on the interior of the combustion chamber.

The data from these runs were also plotted with the logarithm of ignition delay against the reciprocal of absolute temperature (fig. 6). With the acid containing 2 percent water, the resulting curve is a straight horizontal line since the temperature coefficient was zero in the range investigated. With the acid containing 5 percent water, no satisfactory curve could be drawn through the data points. With the acid containing 16 percent water, an approximate linear relation was found to exist.

Mixed Butyl Mercaptans - White Fuming Nitric Acid

Modified open-cup. - A summary of the data obtained with the modified open-cup apparatus using mixed butyl mercaptans and white fuming nitric acid (USAF Specification No. 14104) has been reported previously (ref. 1) and is shown in table III.

Twelve runs were made with a fuel-oxidant weight ratio of 0.30 in each case. The ignition delay increased with a decrease in temperature, ranging from an average of about 55 milliseconds at 21.5° C to 110 milliseconds or infinity (no ignition) at -18.5° C. A nondestructive explosion accompanied each ignition. In four trials, no ignition was obtained at -38.5° C.

When the logarithm of the ignition delay is plotted against the reciprocal of absolute temperature, an approximate linear relation is obtained, as shown by the solid line in figure 7. This does not take into account the infinitely long delays (no ignition) at -18.5° C and -38.5° C.

Small-scale engine. - A summary of the data obtained with the small-scale rocket-engine apparatus using the same propellant combination was also reported previously (ref. 1) and is shown in table IV.

2974 A total of 13 runs was made with 5 resulting in explosions. With the exception of two runs that resulted in doubtful ignitions (runs 199 and 201), the delay of all the measured runs at room temperature and pressure and at fuel-oxidant weight ratios from 0.2 to 0.4 was 38 ± 4 milliseconds. Each one had a hard start. All the remaining runs at reduced temperatures and pressures were terminated by explosions. The average ignition delay for runs at room temperature and 50 millimeters of mercury was 84 milliseconds. Two runs were made at -38°C and sea-level pressure. After long delays of at least 400 milliseconds, both runs resulted in destructive explosions.

The data for the runs at sea-level pressure were plotted with the logarithm of the ignition delay as a function of the reciprocal of absolute temperature (fig. 7). Since it has been shown by experience that the modified open-cup usually yields ignition delays that are equal to or longer than those obtained with the small-scale engine for the same propellant combinations at the same conditions, it is possible that the slopes of the two curves in figure 7 are approximately equal and linear from room temperature to about -20°C , and nonlinear below -20°C , as indicated by the dotted lines.

SUMMARY OF RESULTS

Ignition-delay determinations of furfuryl alcohol and mixed butyl mercaptans with various white fuming nitric acids were made at several temperatures utilizing a modified open-cup apparatus and a small-scale rocket engine of approximately 50-pounds thrust. The results of these experiments are summarized as follows:

1. With furfuryl alcohol and a white fuming nitric acid containing about 2 percent water by weight, the average ignition delay in the modified open-cup apparatus was constant and equal to about 25 milliseconds from 22° to 2°C . With the same fuel and a similar acid, the average ignition delay in the small-scale rocket engine was also constant and equal to about 16 milliseconds from 50° to -20°C .
2. With furfuryl alcohol and white fuming nitric acids containing less than 1 percent water by weight, the ignition delays at -40°C were about 49 milliseconds (average) in the modified open-cup apparatus and 54 milliseconds in the small-scale engine.
3. With furfuryl alcohol and a white fuming nitric acid containing about 5 percent water by weight, the ignition delays in the small-scale engine ranged from 18 milliseconds at 30°C to 70 milliseconds at -40°C .
4. With furfuryl alcohol and a white fuming nitric acid containing about 16 percent water by weight, the ignition delays in the small-scale engine ranged from 43 milliseconds at 19°C to 225 milliseconds at -20°C .

5. With mixed butyl mercaptans and a white fuming nitric acid containing 2 percent water by weight in the modified open-cup apparatus, the ignition delays (about 55 millisecond at 21.5°C) increased with decreasing temperature until no ignition could be obtained at -38.5°C . A nondestructive explosion accompanied each ignition. With the same propellant combination in the small-scale engine, the ignition delay of all measured runs (except two that resulted in doubtful ignitions) at room temperature and pressure, and at various fuel-oxidant weight ratios was 38.4 milliseconds. All runs at reduced temperatures and pressures were terminated by explosions.

6. Plots of the logarithm of ignition delay against the reciprocal of absolute temperature yield approximate linear relations for furfuryl alcohol and white fuming nitric acid (16 percent water) in the small-scale engine and for mixed butyl mercaptans and white fuming nitric acid (2 percent water) in the modified open-cup apparatus for the temperature ranges investigated. Similar plots for furfuryl alcohol and white fuming nitric acid (2 percent water) in both apparatus yield straight horizontal lines since the temperature coefficient of ignition delay is zero for the ranges investigated. Similar plots for furfuryl alcohol and white fuming nitric acid (5 percent water) and mixed butyl mercaptans and white fuming nitric acid (2 percent water) in the small-scale engine were inconclusive with respect to the shape of the curves.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, June 1, 1953

REFERENCES

1. Ladanyi, Dezo J., and Miller, Riley O.: Comparison of Ignition Delays of Several Propellant Combinations Obtained with Modified Open-Cup and Small-Scale Rocket Engine Apparatus. NACA RM E53D03, 1953.
2. Miller, Riley O.: Low-Temperature Ignition-Delay Characteristics of Several Rocket Fuels with Mixed Acid in Modified Open-Cup-Type Apparatus. NACA RM E50H16, 1950.
3. Miller, Riley O.: Ignition-Delay Characteristics in Modified Open-Cup Apparatus of Several Fuels with Nitric Acid Oxidants within Temperature Range 70° to -105°F . NACA RM E51J11, 1951.
4. Ladanyi, Dezo J.: Ignition Delay Experiments with Small-Scale Rocket Engine at Simulated Altitude Conditions Using Various Fuels with Nitric Acid Oxidants. NACA RM E51J01, 1952.

TABLE I. - SUMMARY OF DATA OBTAINED WITH MODIFIED OPEN-CUP APPARATUS

[Furfuryl alcohol and white fuming nitric acids]

Propellant temperature, °C	Ignition delay, millisec
Acid with 2 percent water by weight	
22	26
22	24
21.5	29
21.5	23
9	26
9	21
8.5	28
2	42
2	29
2	25
2	22
2	21
Acid with <1 percent water by weight	
-40	^a 48.5

^aAverage of 14 runs ranging from 30 to 72 milliseconds.

TABLE II. - SUMMARY OF DATA OBTAINED WITH SMALL-SCALE ROCKET ENGINE APPARATUS

[Furfuryl alcohol and several white fuming nitric acids]

Run	Average propellant tempera- ture, °C	Maximum combustion- chamber pressure, lb/sq in. gage	Time to attain maximum combustion- chamber pressure, -sec	Temperature, °C						Lead propellant into com- bustion chamber	Time between jet entries into combustion chamber, millisec	Ignition delay, millisec
				Oxidant	Fuel	Injector head	Constant tempera- ture bath	Nozzle plate	Ambient air			
Acid with < 1 percent water by weight												
73	-40.0	a170	b3.4	----	-40	-36.1	-40.6	12.2	17.2	Oxidant	63.3	53.7
Acid with 2 percent water by weight												
320	50.0	285	0.6	50.0	50.0	51.7	51.1	30.6	30.0	Fuel	0.2	15.6
313	40.6	290	.7	40.6	40.6	41.1	41.1	23.9	25.6	Oxidant	.6	18.1
321	30.3	280	.6	30.0	30.6	30.0	30.0	20.6	18.3	Oxidant	24.2	18.9
314	19.7	230	.6	20.0	19.4	20.0	19.4	25.6	27.8	Fuel	8.1	14.8
322	10.0	297	.6	10.0	10.0	10.6	10.6	23.3	19.4	Fuel	14.9	15.4
323	-0.3	280	.6	0.0	-0.6	0.6	0.0	20.6	25.0	Oxidant	5.0	13.1
324	-19.7	270	.6	-20.0	-19.4	-19.4	-19.4	16.1	26.7	Oxidant	20.2	16.9
Acid with 5 percent water by weight												
298	30.0	200	0.4	30.0	30.0	30.0	29.4	20.0	17.8	Oxidant	2.7	18.1
297	9.4	190	.5	9.4	----	9.4	9.4	17.2	22.2	Fuel	18.4	18.1
296	-10.6	(c)	(c)	-10.6	----	-10.0	-10.6	11.7	13.9	Oxidant	25.8	58.8
294	-40.0	80	.6	-40.0	----	-39.4	-41.1	13.9	12.8	Oxidant	40.5	69.9
Acid with 16 percent water by weight												
299	19.4	187	0.4	19.4	19.4	20.0	20.0	24.4	25.6	Fuel	8.6	42.7
300	0.0	150	.5	0.0	0.0	0.6	0.6	22.2	21.7	Oxidant	9.4	84.8
301	-20.3	113	.3	-20.0	-20.6	-18.3	-18.9	17.8	20.0	Fuel	11.4	225

^aPeak pressure; maximum pressure possible was probably not attained.^bTime to attain peak combustion-chamber pressure.^cNo chamber-pressure record.

TABLE III. - SUMMARY OF DATA OBTAINED WITH MODIFIED OPEN-CUP APPARATUS

[Mixed butyl mercaptans and white fuming nitric acid containing
2 percent water by weight, ref. 1]

Propellant temperature, °C	Fuel quantity, ml	Oxidant quantity, ml	Fuel- oxidant weight ratio	Ignition delay, millisec
21.5	1.4	2.6	0.30	^a 52
21.5	1.4	2.6	.30	^a 57
3.0	1.4	2.6	.30	^a 63
3.0	1.4	2.6	.30	^a 70
2.1	1.4	2.6	.30	^a 85
-18.5	1.4	2.6	.30	^a 110
-18.5	1.4	2.6	.30	No ignition
-18.5	1.4	2.6	.30	No ignition
-38.5	1.4	2.6	.30	No ignition
-38.5	1.4	2.6	.30	No ignition
-38.5	1.4	2.6	.30	No ignition
-38.5	1.4	2.6	.30	No ignition

^aNondestructive explosion accompanied ignition.



TABLE IV. - SUMMARY OF DATA OBTAINED WITH SMALL-SCALE ROCKET ENGINE APPARATUS
 [Mixed butyl mercaptans and white fuming nitric acid containing 2 percent water by weight, ref. 1]

Run	Average pro- pellant tempera- ture, °C	Initial ambient pressure, mm Hg	Maximum combustion chamber pressure, lb/sq in. gage	Time to attain maximum combustion chamber pressure, sec	Temperature, °C						Lead propellant into com- bustion chamber	Time between jet entries into com- bustion chamber, millisec	Time between ignition and ex- plosion, millisec	Fuel- oxidant weight ratio	Ignition delay, millisec
					Oxidant	Fuel	Injector head	Constant tempera- ture bath	Nozzle plate	Ambient air					
195	22.2	~760	280	1.3	22.2	22.2	22.2	22.2	20.6	22.2	Oxidant	0.6		0.30	35.0
196	22.2	~780	315	1.2	22.2	22.2	22.2	22.8	20.8	22.8	Fuel	13.2		.30	41.4
202	-37.8	~760	(b)	(b)	-37.8	---	-36.7	-37.8	11.7	17.2	Fuel	0.3	0.7	0.30	406
219	-37.8	~760	(b)	(b)	-37.8	-37.8	-37.2	-37.8	13.3	18.3	Fuel	.8	(c)	.30	d, 575
200	21.7	48.8	(b)	(b)	21.7	21.7	21.7	22.2	18.9	21.7	Fuel	3.4	0.8	0.30	72.5
211	22.2	50.0	(b)	(b)	22.2	22.2	22.2	22.2	18.9	20.0	(e)	(e)	(e)	.30	(e)
212	22.2	49.5	(b)	(b)	22.2	22.2	21.7	22.2	19.4	19.4	Fuel	7.4	4.2	.30	95.3
197	22.5	~760	315	1.5	22.2	22.8	22.8	22.8	21.1	22.2	Oxidant	0.6		0.40	37.5
198	22.2	~780	310	1.5	22.2	22.2	22.2	22.2	21.1	23.3	Oxidant	1.6		.40	38.8
199	22.2	~780	(f)	(f)	22.2	22.2	22.2	22.2	20.0	21.1	Fuel	3.6		.20	d, 536
201	22.2	~780	(f)	(f)	22.2	22.2	22.2	22.2	21.1	22.2	Fuel	.5		.20	d, 510
213	22.0	~780	180	1.6	22.2	21.7	22.8	---	22.2	23.3	(i)	(i)		.20	(i, j)
214	22.2	~760	180	1.0	22.2	22.2	22.2	22.2	21.1	22.2	Oxidant	.6		.20	34.4

^aHeavy cylindrical steel shield slipped over plastic combustion chamber to contain explosion.

^bExplosion.

^cExplosion occurred after end of film roll.

^dIgnition occurred after end of film roll.

^eNo photographic records because of defective electric system.

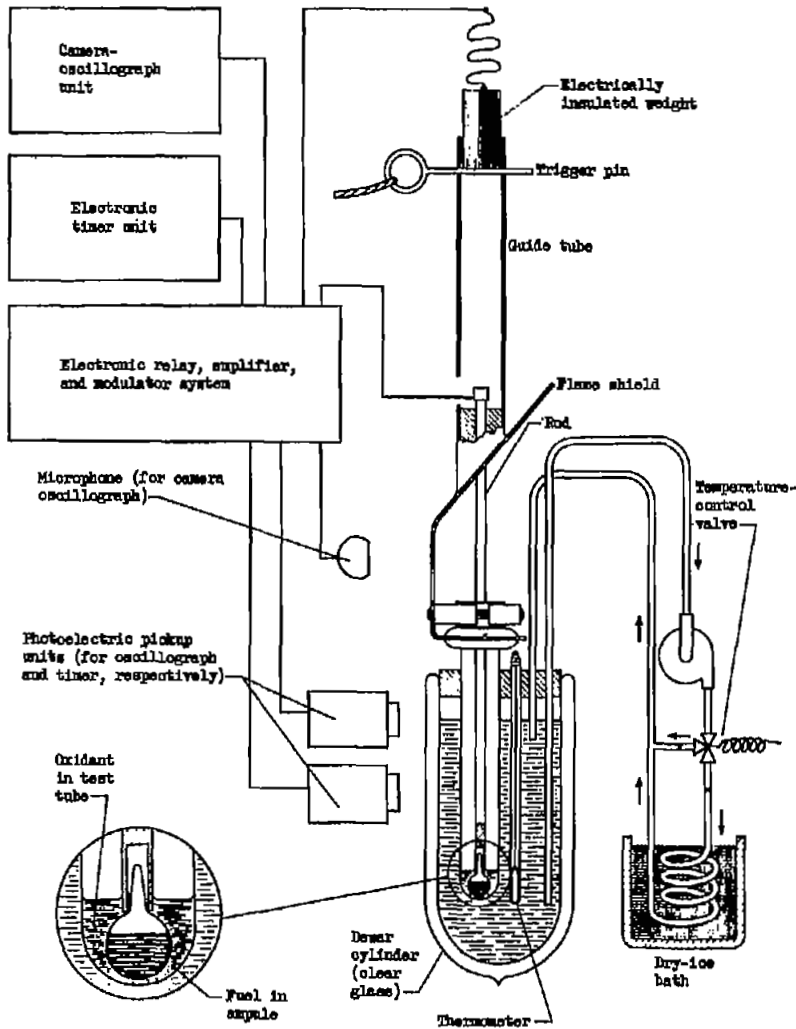
^fRestriction in line from combustion chamber to pressure recorder.

^gDoubtful ignition.

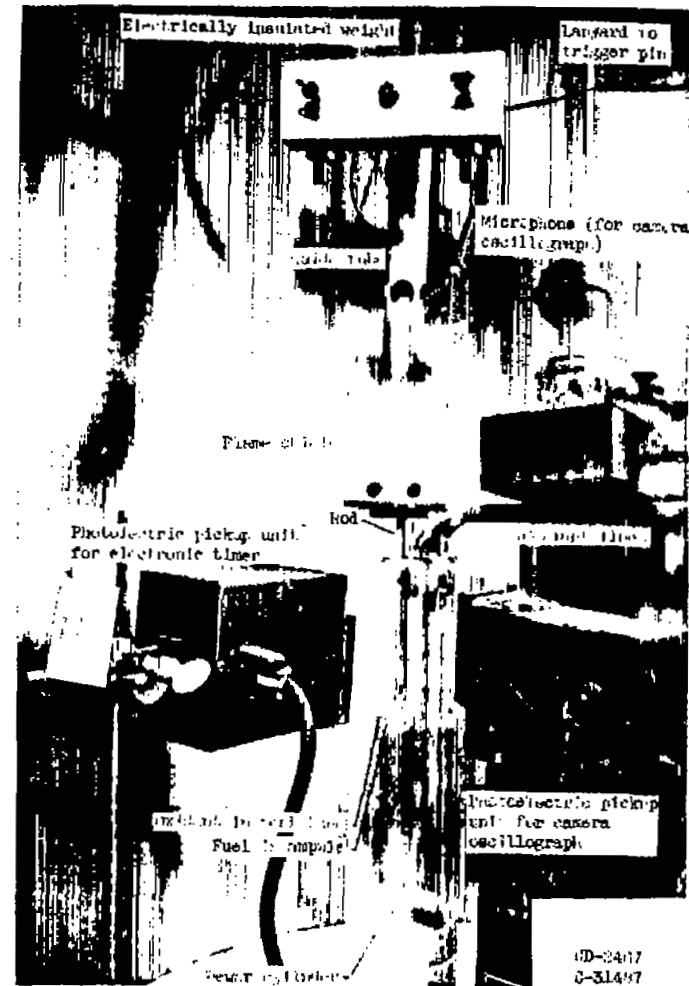
^hRun made in complete darkness for visual check of doubtful ignitions of runs 199 and 201.

ⁱNo film records made.

^jPositive ignition, observed audibly and visually.

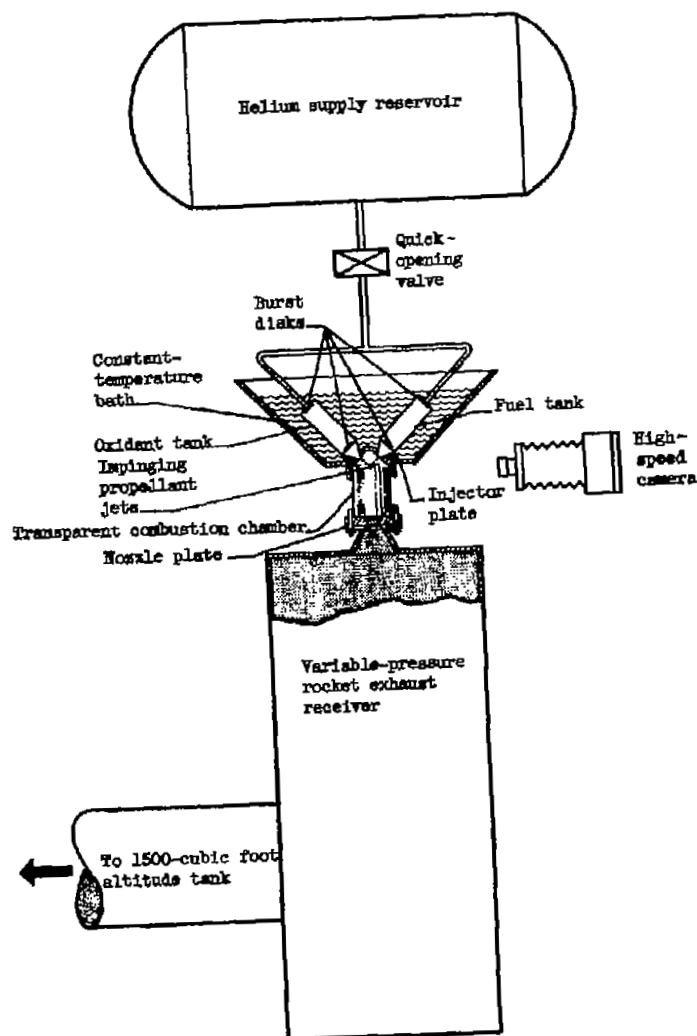


(a) Diagrammatic sketch.

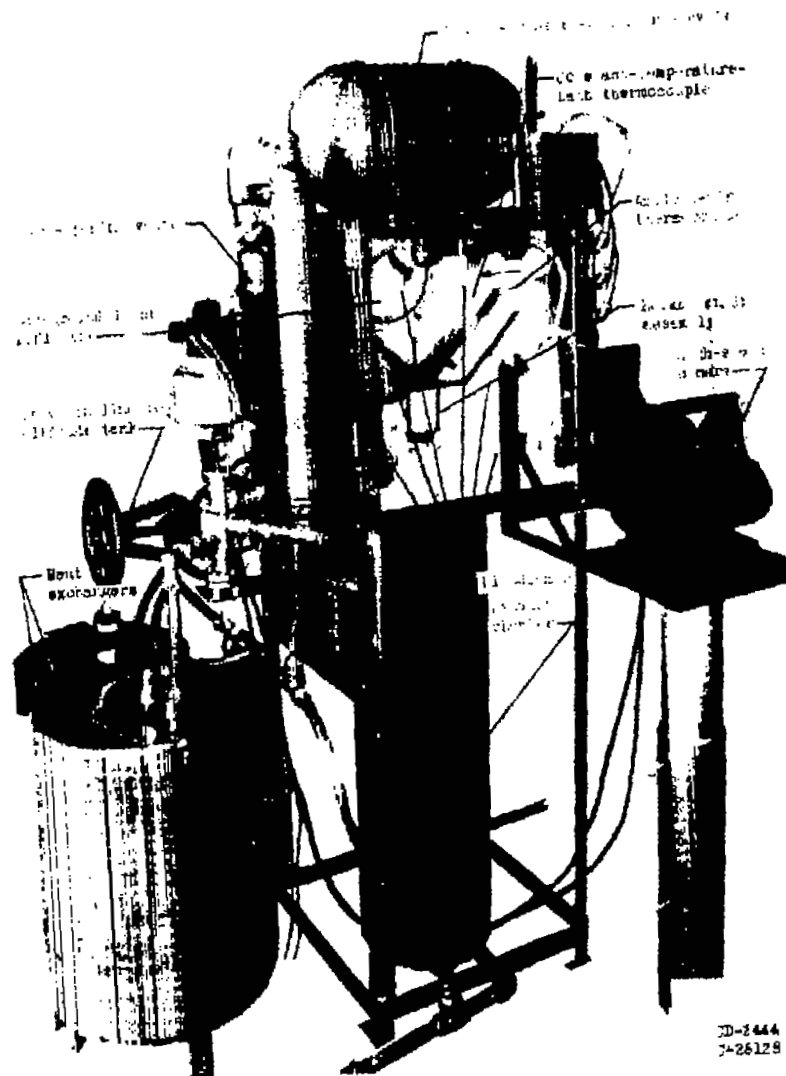


(b) Photograph of assembly.

Figure 1. - Modified open-cup ignition-delay apparatus.



(a) Diagrammatic sketch.



(b) Photograph of assembly.

Figure 2. - Small-scale rocket engine ignition-delay apparatus.

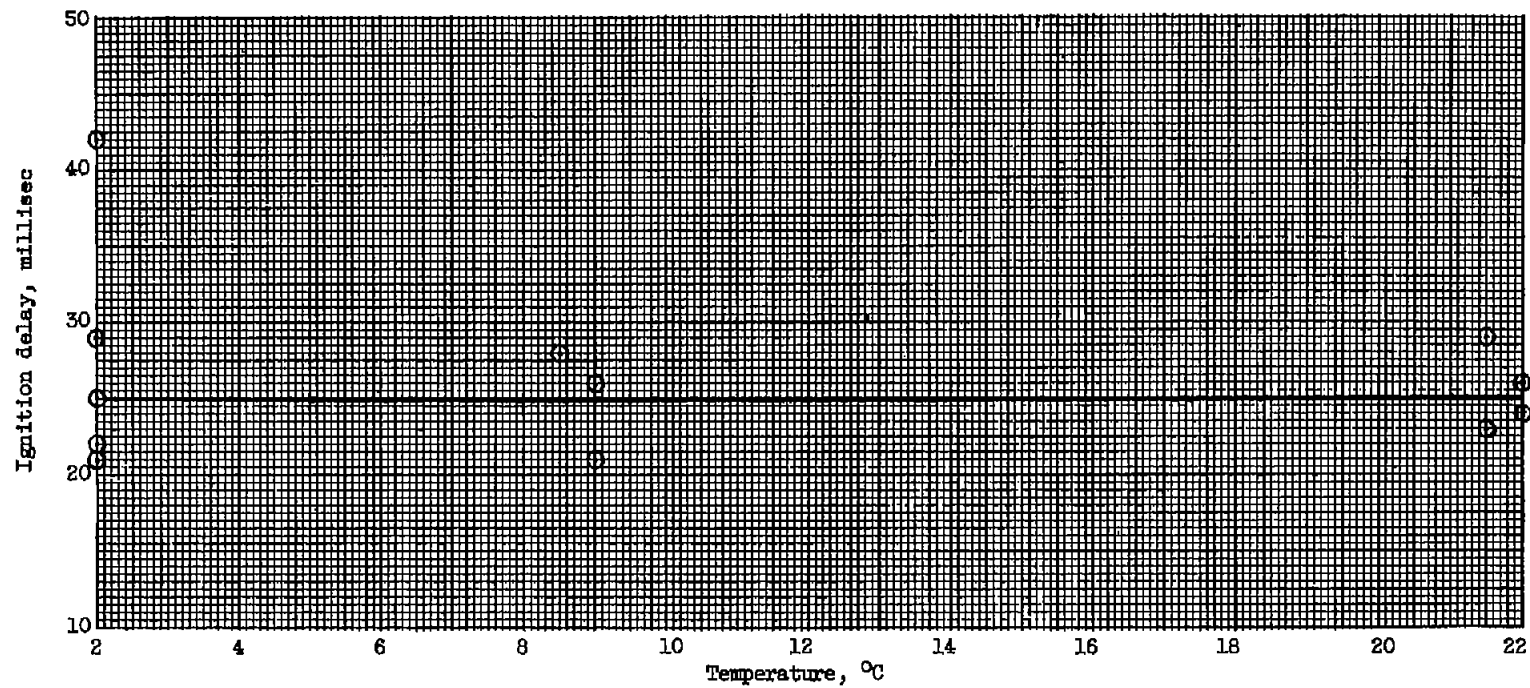


Figure 3. - Ignition delay of furfuryl alcohol and white fuming nitric acid containing 2 percent water by weight (modified open-cup apparatus).

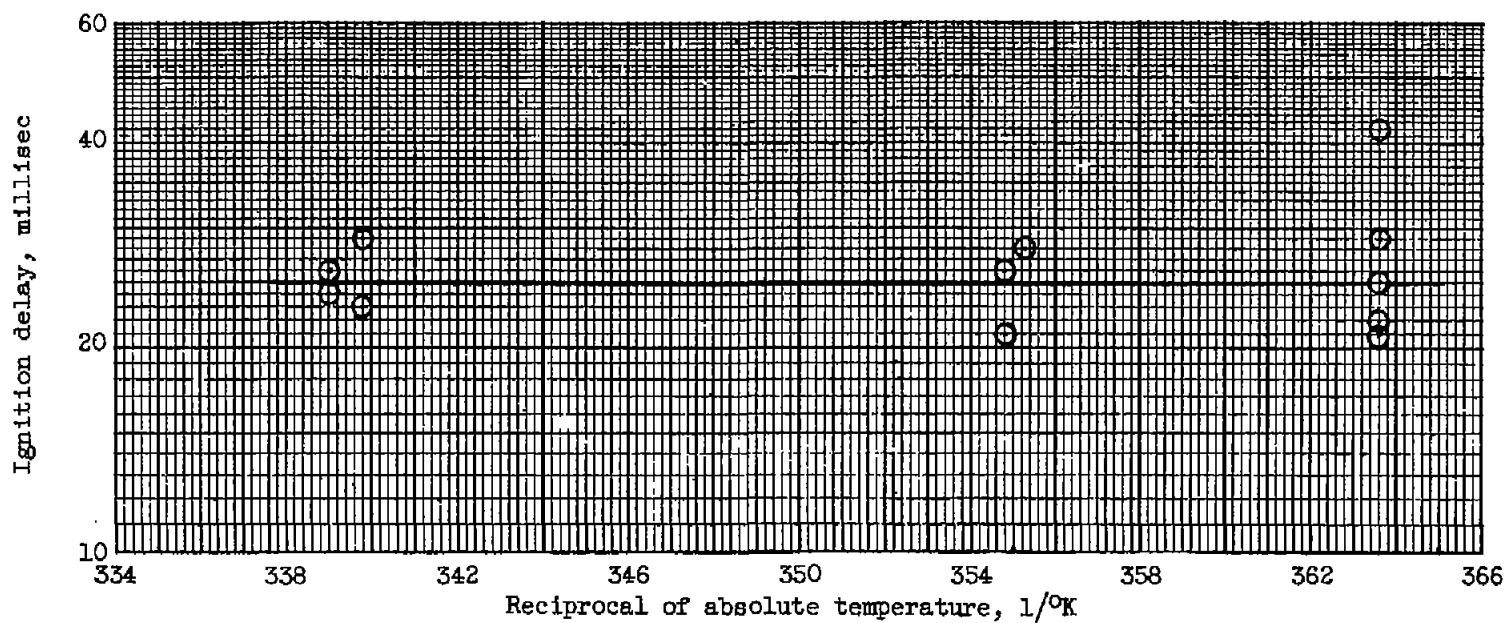


Figure 4. - Logarithm of ignition delay against reciprocal of absolute temperature for furfuryl alcohol and white fuming nitric acid containing 2 percent water by weight (modified open-cup apparatus).

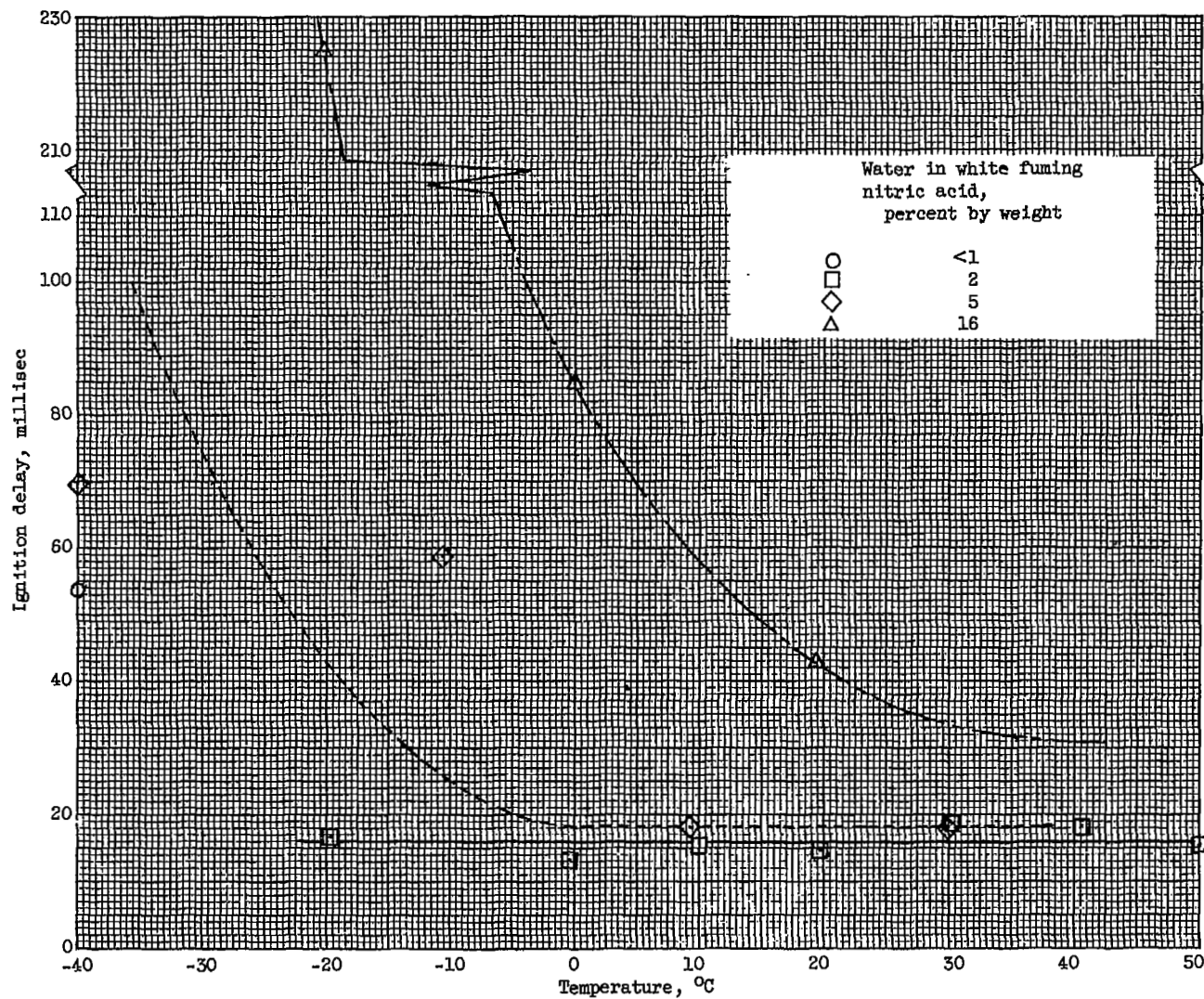


Figure 5. - Ignition delay of furfuryl alcohol and several white fuming nitric acids (small-scale rocket engine apparatus).

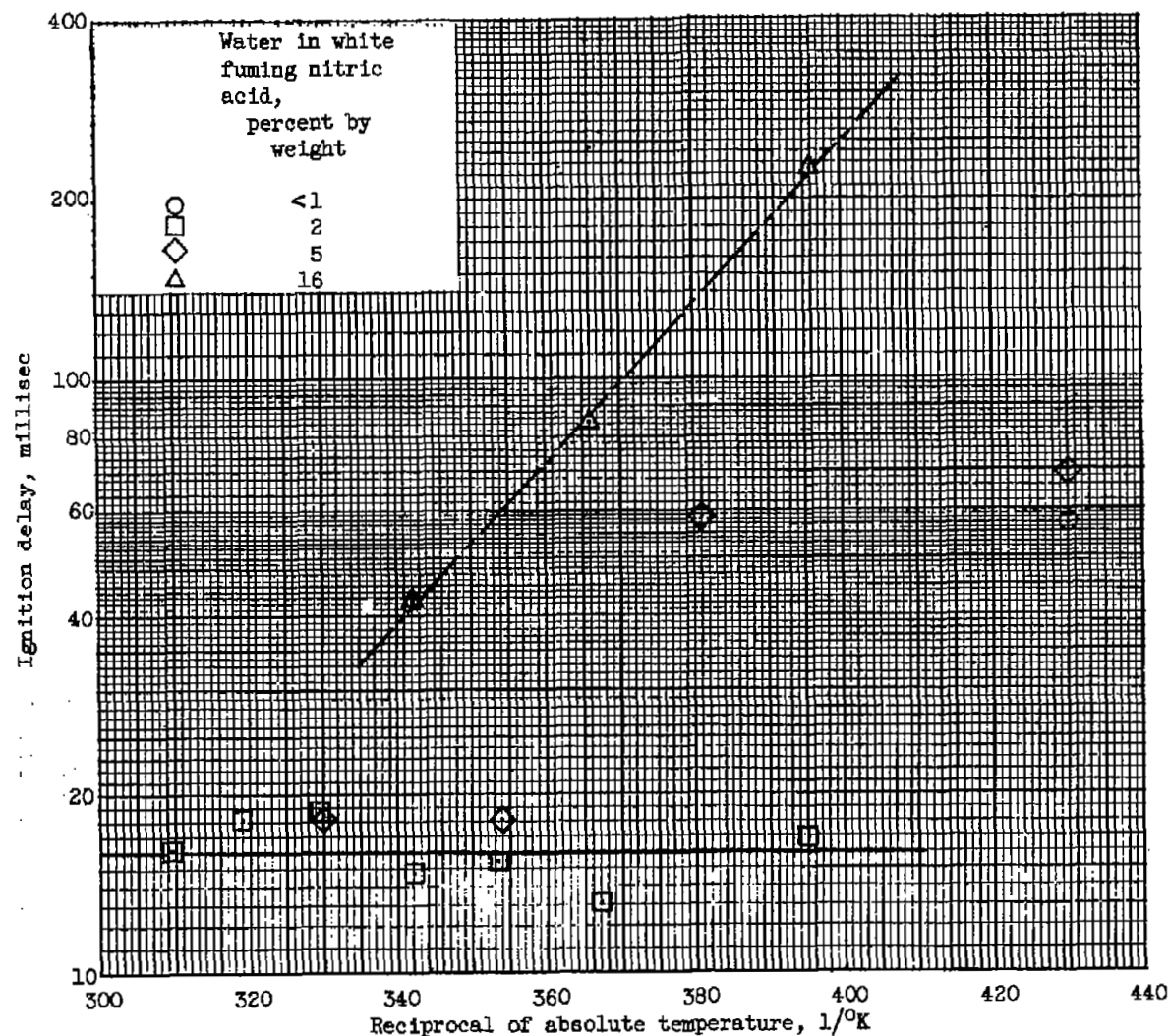


Figure 6. - Logarithm of ignition delay against reciprocal of absolute temperature for furfuryl alcohol and several white fuming nitric acids (small-scale rocket engine apparatus).

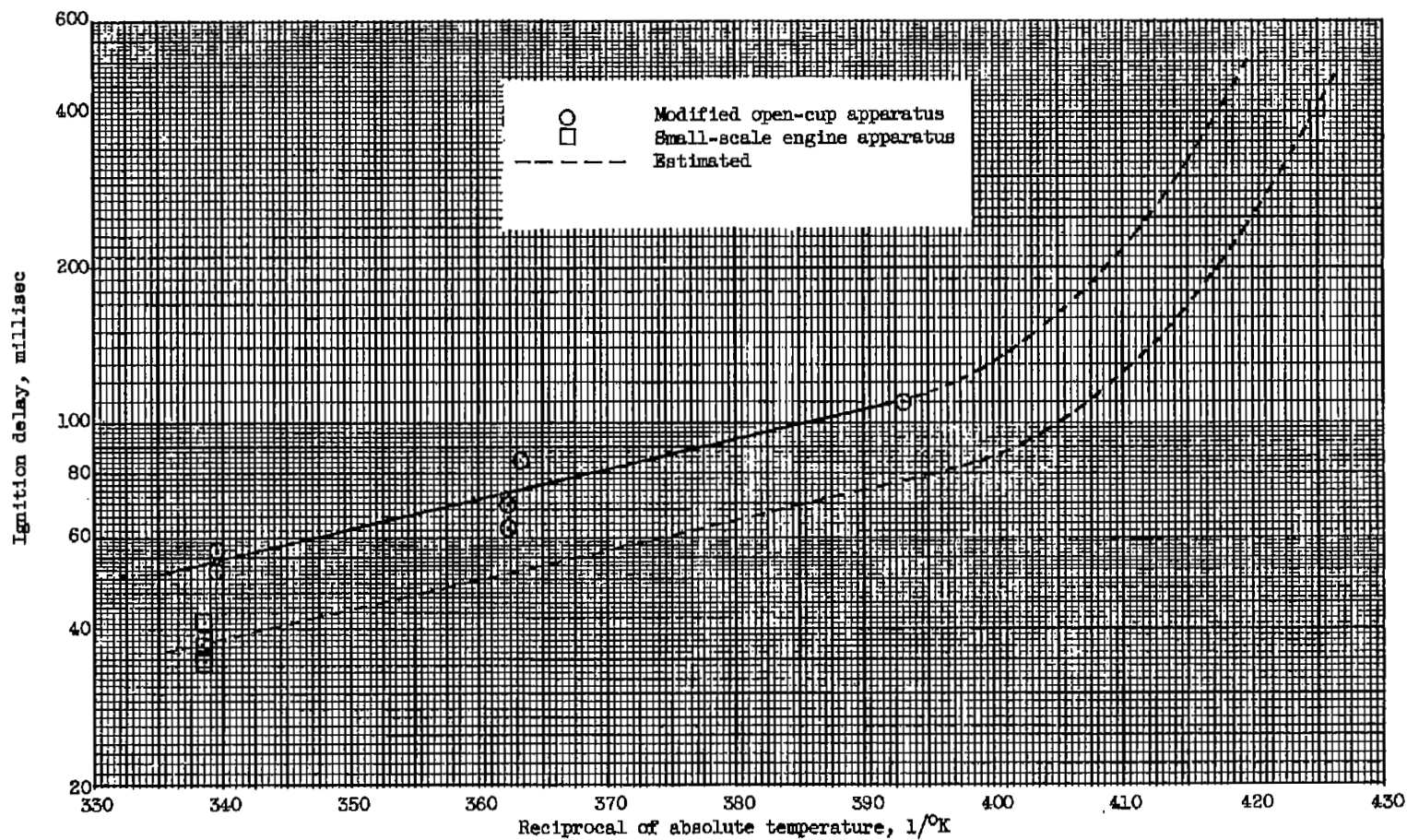


Figure 7. - Logarithm of ignition delay against reciprocal of absolute temperature for mixed butyl mercaptans and white fuming nitric acid containing 2 percent water by weight.



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